DOI 10.1007/s10717-014-9666-2
Glass and Ceramics, Vol. 71, Nos. 7 – 8, November, 2014 (Russian Original, Nos. 7 – 8, July – August, 2014)

GLASS CERAMICS

UDC 666.1:535.372

YELLOW UP-CONVERSION LUMINESCENCE OF TRANSPARENT GLASS CERAMICS WITH ERBIUM IONS

G. E. Rachkovskaya,[1, 3] P. A. Loiko,[2] N. A. Skoptsov,[2] G. B. Zakharevich,[1] and K. V. Yumashev[2]

Translated from *Steklo i Keramika*, No. 8, pp. 6 – 9, August, 2014.

A transparent glass ceramic, containing lead fluoride β-PbF_2 nanocrystals with erbium ions Er^{3+} (average diameter 8.5 nm), was synthesized by means of secondary thermal treatment of the initial oxyfluoride glass of the system SiO_2–GeO_2–PbO–PbF_2, doped with Er_2O_3. Its thermal and structural properties, optical absorption, and up-conversion luminescence were studied. The glass ceramic obtained holds promise as a luminophore and makes it possible to obtain intense yellow luminescence by excitation in the IR range of the spectrum.

Key words: transparent glass ceramics, erbium ions, lead fluoride, up-conversion, luminescence.

Oxyfluoride glasses containing erbium ions Er^{3+} are attractive as luminophores in the green region of the spectrum [1]. This is due to the presence of efficient up-conversion processes which result in the light emission near the wavelengths 520 and 550 nm (transitions from the levels $^2H_{11/2}$ and $^4S_{3/2}$ into the ground state $^4I_{1/2}$) as a result of excitation in the infrared region of the spectrum [2]. Powerful, commercially available InGaAs laser diodes (960 – 980 nm) are used for this. The oxyfluoride matrix of the glass also combines good mechanical and thermal properties of oxide glasses with low-energy phonons of fluoride materials (this substantially improves the luminescence properties) [3]. In addition, lead-containing oxyfluoride glasses have the advantage of melting easily: the synthesis temperature is 900 ± 50°C.

A drawback of oxyfluoride glasses with respect to the common luminophores based on nanopowders of fluoride and oxide crystals is the low admissible concentration of rare-earth ions [4]. Specifically, when such ions are introduced in the form of the fluorides REF_3 or oxides RE_2O_3 the concentration does not exceed 2 – 3 mol.%. One way suggested to solve this problem is controlled growth of fluoride nanocrystals (5 – 50 nm) in the oxide matrix of the glass under the secondary heat treatment used in this method [1]. In this case the transparency of the glass ceramic obtained is preserved and the mechanical properties of the ceramic are improved. This makes it possible to form a two-phase material with a high local concentration of ions in nanocrystals, which greatly intensifies (by more than a factor of 10) the up-conversion luminescence [5].

A known mechanism for intensifying the absorption of the exciting light is co-activation of glasses and glass ceramic by Er^{3+} and Yb^{3+} ions (the latter act as sensitizers). At the same time the reagents YbF_3 and Yb_2O_3 usually contain uncontrollable thulium impurities, whose 'parasitic' luminescence in the blue region (480 nm) distorts the color characteristics of the material. On the other hand, clusterization of Yb^{3+} ions is observed for high local concentrations, which also decreases the efficiency of the green luminescence via the mechanism of cooperative relaxation [6]. Thus, there is promise in studying materials containing only Er^{3+} ions. The drawback of such materials is weak absorption near 960 nm, which can be eliminated by optimizing the glass composition.

The most common nanocrystalline phases in oxyfluoride glass ceramics are low-phonon (337 cm^{-1}) crystals of lead fluoride PbF_2 [1 – 5]. This compound can form stable solid solutions with erbium fluoride ErF_3 with molar content up to 40 mol.%. At present the best studied glasses from the standpoint of the crystallization of the nanophase PbF_2 are the two-component glasses in the system (mol.%) 50 SiO_2 –

[1] Belorussian State Technological University, Minsk, Belarus.
[2] Belorussion National Technical University, National Scientific Center for Optical Materials and Technologies, Minsk, Belarus.
[3] E-mail: rach_halina@mail.ru.

50 PbF_2 [1, 3]. At the same time it is of great interest to look for new matrices with improved luminescence properties. Specifically, glasses modified by germanium oxide GeO_2 are being studied [4, 7].

In the present article we present the results on the synthesis and investigation of the structural properties, optical absorption and up-conversion of the luminescence of glass ceramic, obtained on the basis of lead-silicon-germanate glass, with lead difluoride nanocrystals $Er : PbF_2$ containing erbium ions. The idea of this work consists in controllable intensification of red luminescence of Re ions near 650 nm in order to obtain promising yellow luminophores.

The initial glass was synthesized in the system SiO_2–GeO_2–PbO–PbF_2 by the conventional glass technology. The main matrix of the glass was activated by erbium oxide Er_2O_3 at molar content 1 mol.%. The glass was synthesized at temperature 950 ± 50°C in an electric furnace in air in 0.5 h. The ready molten glass was extracted onto a smooth metal surface, after which the glass was annealed at temperature about 300°C in an electric muffle furnace and allowed to cool freely to room temperature. XPA confirmed the amorphousness of the initial glass. Next, the glass samples were subjected to secondary heat treatment at temperature 350°C for 10 – 30 h in order to form a transparent glass ceramic. The samples obtained had a rose tint.

Basic Properties of Synthesized Transparent Oxyfluoride Glass Ceramic with Er^{3+} : PbF_2 Nanocrystals

Heat-treatment regime, °C/h	350/30
Density ρ, kg/m^3	6050
CLTE, 10^{-7} K^{-1}	113
Refractive index n	1.61
Band gap E_g, eV	3.58
Average size D of PbF_2 nanocrystals, nm	8.5
PbF_2 lattice parameter a, Å	5.810
Er^{3+} ion concentration in PbF_2 N_{Er}, 10^{-20} cm^{-3}	39
Absorption coefficient α_{abs} at wavelength 972 nm, cm^{-1}	1.66

An investigation of the glasses by differential scanning calorimetry (Fig. 1) showed that the introduction of rare-earth ions Er^{3+} increases the glass formation temperature T_g from 354 to 386°C. Doping the glass matrix with erbium oxide Er_2O_3 gives rise to the nucleation of centers of crystallization and precipitation of the crystal phase of lead fluoride at temperature T_p = 522°C, which attests to an exothermal effect on the DSC curve. The thermal stability index of the glass, defined as the difference $\Delta = T_p - T_g$ = 136°C, is much larger than for the 'conventional' two-component glass SiO_2–PbF_2 (Δ = 56°C) synthesized for comparison. This indicates that the composition chosen is more promising for synthesis of transparent erbium-containing glass ceramic.

The x-ray diffraction pattern of the glass ceramic heat-treated at 350°C in 30 h is presented in Fig. 2. XPA confirms the precipitation of β-PbF_2 nanocrystals (space group Fm3m;

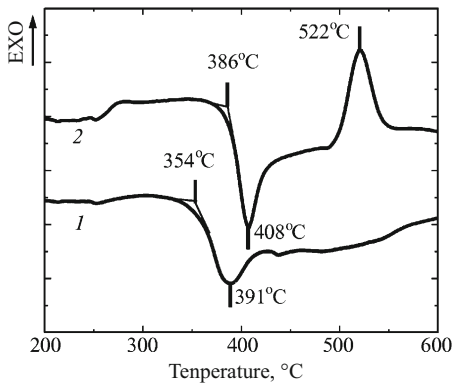

Fig. 1. Differential scanning calorimetry curves for glasses in the system SiO_2–GeO_2–PbO–PbF_2: *1*) nominally pure; *2*) doped with Er_2O_3 (content 1 mol.%).

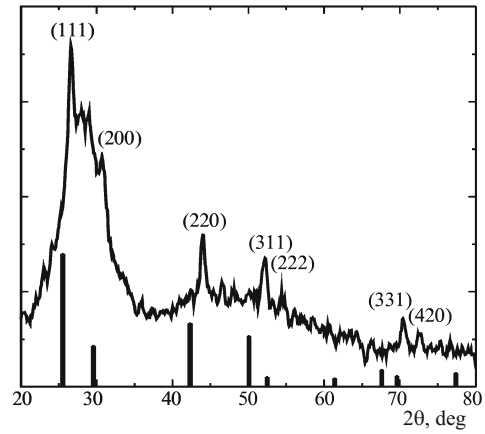

Fig. 2. X-ray diffraction pattern of transparent oxyfluoride glass ceramic with Er^{3+} ions: the vertical lines correspond to the reflections due to a 'bulk' β-PbF_2 crystal; the numbers represent the indices (*hkl*).

the average diameter, calculated using Scherrer's relation, equals 8.5 ± 0.5 nm). The crystallographic reflections of a nominally pure 'bulk' PbF_2 crystal (lattice parameter a = 5.940 Å) are also displayed in the figure.

The diffraction peaks in the x-ray diffraction pattern are shifted relative to these reflections, which attests to distortion of the crystal structure and change in the lattice parameter of the nanocrystals (a = 5.810 Å). This indicates that Er^{3+} ions enter into the crystal lattice of PbF_2. Indeed, the ionic radius of the VIII-coordinated ions Pb^{2+} equals 1.45 Å, which is greater than that of the Er^{3+} ions 1.14 Å). Once the parameter a is determined for nanocrystals the local concentration of erbium oxyfluoride ErOF in the solid solution ErOF–PbF_2 can be determined (Fig. 3). The line corresponds to the data of [8, 9], and the point marks the value obtained in this work. The stoichiometric relation for the nanocrystals formed in the matrix of the glass can be represented in the form $Pb_{0.8}Er_{0.2}O_{0.2}F_{1.8}$ (20 mol.% ErOF).

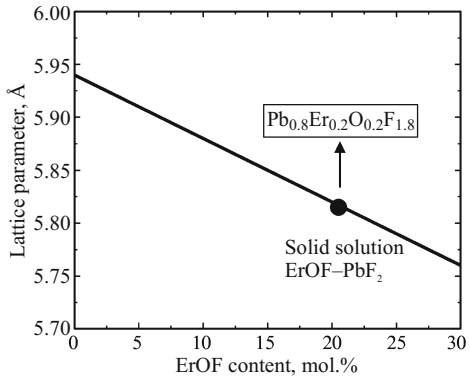

Fig. 3. Crystal lattice parameter of the solid solution ErOF–PbF_2 versus the molar content of ErOF (according to [8, 9]). The point corresponds to the glass ceramic studied; inset: chemical formula for the Er : PbF_2 nanocrystals obtained.

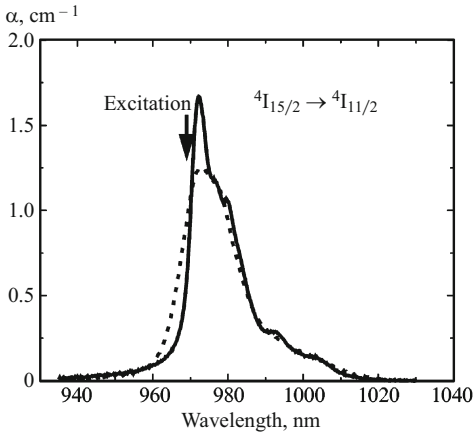

Fig. 4. Structuring of the absorption band of Er^{3+} ions near about 1 μm in the transparent glass ceramic with respect to the initial glass.

The structure of the absorption band of the Er^{3+} ions in the glass and the glass ceramic that is associated with the transition $^4I_{15/2} \rightarrow {}^4I_{11/2}$ is shown in Fig. 4. It is evident that heat-treatment results in structuring of the absorption bands and an increase of the peak in the absorption coefficient to 1.7 cm^{-1} at the wavelength 972 nm, which is sufficient for efficient excitation of luminescence. This confirms that Er^{3+} ions enter into the PbF_2 crystal structure. In addition, the full width of the band at half-height (FWHM) equals 13.7 nm (which is greater than for glass ceramic based on two-component glass SiO_2–PbF_2, where FWHM = 12.5 nm). This makes the glass ceramic less sensitive to the temperature variation of the wavelength of the outgoing radiation of the laser diode.

The up-conversion luminescence spectrum obtained for the glass ceramic by excitation at the wavelength 965 nm is presented in Fig. 5. Intense bands with maxima at the wavelengths 522 nm (transition $^2H_{11/2} \rightarrow {}^4I_{15/2}$) and 540/549 nm (splitting, transition $^4S_{3/2} \rightarrow {}^4I_{15/2}$) – the green part of the

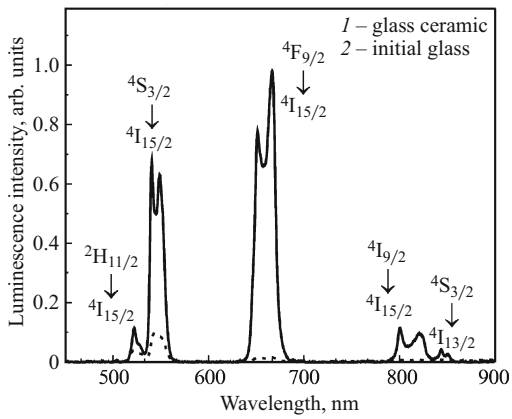

Fig. 5. Yellow up-conversion luminescence spectrum of transparent oxyfluoride glass ceramic with Er^{3+} ions with excitation in the IR range: dashed line) spectrum of the initial glass.

spectrum, 651/667 nm (splitting, transition $^4F_{9/2} \rightarrow {}^4I_{15/2}$) – red part of the spectrum, and 800/821 nm (splitting, transition $^4I_{9/2} \rightarrow {}^4I_{15/2}$) – IR region are observed in the spectrum.

The intensity of the 'red' luminescence was comparable to that of the 'green' luminescence. This determines the saturated yellow color of the emission, in contrast to the initial glass with green emission (the corresponding spectrum is shown by the dashed line in Fig. 5). The change in the ratio of the 'green' and 'red' luminescence on heat treatment of the initial glass is related mainly with the increase in the local concentration of Er^{3+}ion in PbF_2 nanocrystals to 39×10^{20} cm^{-3} (for the initial glass it equals 4.4×10^{20} cm^{-3}). This leads to a reduction of the lifetime of the $^4I_{11/2}$ and $^4I_{13/2}$ levels (in addition, for the $^4I_{11/2}$ level the lifetime decreases much more rapidly, so that the relative intensity of the 'green' luminescence decreases).

Heat treatment of the initial glass also results in a significant increase in the intensity of the up-conversion luminescence (by approximately a factor of 10). This is associated with, in the first place, the change in the local environment of the Er^{3+} ions from oxyfluoride to fluoride and, correspondingly, to a large decrease in the phonon energy, which determines the intensification of the radiative transitions. In the second place, the average distances between the ions Er^{3+}–Er^{3+} in nanocrystals decrease significantly compared with the initial glass, which results in an intensification of the energy transfer processes responsible for the up-conversion transformation.

In summary, the results on the synthesis, investigation of the thermal and structural properties, and the optical absorption and up-conversion of the luminescence of transparent glass ceramic (with Er : PbF_2 nanocrystals) obtained in the process of heat treatment of oxyfluoride glass in the system SiO_2–GeO_2–PbO–PbF_2 were presented. The glass ceramic possesses improved absorption and luminescence properties with respect to glass ceramic based on the 'standard' glass

matrix SiO_2–PbF_2 and is promising as a luminophore in the yellow region of the spectrum.

REFERENCES

1. M. J. Dejneka, "The luminescence and structure of novel transparent oxyfluoride glass-ceramics," *J. Non-Cryst. Solids*, **239**, 149 – 155 (1998).
2. M. Takahashi, M. Izuki, R. Kanno, et al., "Up-conversion characteristics of Er^{3+} in transparent oxyfluoride glass–ceramics," *J. Appl. Phys.*, **83**, 3920 (1998).
3. P. A. Loiko, G. E. Rachkovskaya, G. B. Zakharevich, and K. V. Yumashev, "New luminescing oxyfluoride glass with europium and ytterbium ions," *Steklo Keram.*, No. 2, 3 – 6 (2014); P. A. Loiko, G. E. Rachkovskaya, G. B. Zakharevich, and K. V. Yumashev, "New luminescing oxyfluoride glass with europium and ytterbium ions," *Glass Ceram.*, **71**(1 – 2), 41 – 44 (2014).
4. L. A. Bueno, P. Melnikov, Y. Messaddeq, et al., "Er^{3+} and Eu^{3+} containing transparent glass ceramics in the system $PbGeO_3$–PbF_2–CdF_2," *J. Non-Cryst. Solids*, **247**, 87 – 91 (1999).
5. X. Qiao, X. Fan, M. Wang, et al., "Up-conversion luminescence and near infrared luminescence of Er^{3+} in transparent oxyfluoride glass-ceramics," *Opt. Mater.*, **27**, 597 – 603 (2004).
6. F. Auzel and P. Goldner, "Towards rare-earth clustering control in doped glasses," *Opt. Mater.*, **16**, 93 – 103 (2001).
7. Z. Pan, A. Ueda, M. Hay, et al., "Studies of Er^{3+} doped germinate-oxyfluoride and tellurium-germanate-oxyfluoride transparent glass-ceramics," *J. Non-Cryst. Solids*, **352**, 801 – 806 (2006).
8. G. Dantelle, M. Mortier, G. Patriarche, et al., "Er^{3+}-doped PbF_2: comparison between nanocrystals in glass-ceramics and bulk single crystals," *J. Solid-State Chem.*, **179**, 1995 – 2003 (2006).
9. M. Mortier, P. Goldner, C. Chateau, et al., "Erbium doped glass-ceramics: concentration effect on crystal structure and energy transfer between active ions," *J. Alloys Compound*, **323 – 324**, 245 – 249 (2001).